APPLICABILITY OF COMMERCIALLY AVAILABLE SLAG MODELS FOR STEEL MAKING SLAG

Somnath Basu
Tata Steel Limited, India

Ashok Kumar Lahiri
Independent Consultant, India

Seshadri Seetharaman
Royal Institute of Technology, Sweden

ABSTRACT

The activities of three common constituents of steel making slag, viz. FeO, P_2O_5 and Fe_2O_3, were estimated using some of the commercially available thermodynamic packages, which are based on different slag models. The results were compared with experimentally measured values. It was observed that the activities of FeO, calculated using the package ThermoCalc™, were of the same order of magnitude as the measured values. The deviations were much larger for a (Fe_2O_3) and most pronounced for $a(P_2O_5)$. The difference between computed and measured activity values, even for FeO, has been found to be non-random. The effect of different parameters on the magnitude of deviation has been investigated.

INTRODUCTION

Manufacture of steel involves, to a large extent, oxidation of impurity elements from liquid metal. The products of oxidation, in most cases, join the slag phase which remains in contact with liquid steel throughout the refining process. The extent of refining, therefore, depends strongly on the activities of the various oxides involved.

The activities of FeO, Fe_2O_3 and P_2O_5 were measured by the authors recently [1, 2]. The activities were simultaneously estimated through the use of commercially available thermodynamic softwares, corresponding to the chemical compositions encountered in the experiments. The results of the computations were observed to differ, often substantially, from the measured values. It was therefore felt necessary to explore the nature of deviation for different oxide species involved, and also to attempt a comparison between the different thermodynamic softwares in terms of the reliability of estimation for the respective oxides.

METHODOLOGY

The details of the experiments for measurement of $a(\mathrm{FeO})$, $a(Fe_2O_3)$ and $a(P_2O_5)$ have been described elsewhere [1, 2, 3]. The activity of FeO was calculated from the oxygen content in liquid iron held in equilibrium with FeO-containing slag, using the following relation.

$$\mathrm{Fe}\,(l) + [\mathrm{O}] = \mathrm{FeO}\,(l) \qquad (1)$$

$$\Delta G° = -\ 121983.61\ \mathrm{w} +\ 52.26\ \mathrm{T}\ (\mathrm{J\ mol^{-1}})$$

$$= -\ RT \ln \{a(\mathrm{FeO})/h_{[\mathrm{O}]}\}$$

$$a(\mathrm{FeO}) = h_{[\mathrm{O}]} \times \exp(-\Delta G°/RT)$$

$$h_{[\mathrm{O}]} = [\mathrm{mass\%\ O}] \times f_{\mathrm{O}}, \text{ where}$$

$$\log_{10} f_{\mathrm{O}} = \Sigma\, e_O^i\, .\ [\mathrm{mass\%}\ i] \text{ (neglecting higher order interactions)}$$

Pure liquid iron was considered as the standard state of iron. Those of oxygen and FeO were taken as unit activity coefficient at infinite dilution ($\lim_{[\%\mathrm{O}] \to 0} f_{\mathrm{O}} = 1$) and pure liquid FeO, respectively.

The activities of Fe_2O_3 and P_2O_5 were obtained using the relations (2) and (3). However, for sake of conciseness, the detailed calculations are being omitted here since the same has already been published elsewhere [4, 5].

$$2[\mathrm{P}] + 5[\mathrm{O}] = P_2O_5(l) \qquad (2)$$

$$a(P_2O_5) = h_{[\mathrm{O}]}^5 \times h_{[\mathrm{P}]}^2 \times \exp(-\Delta G°/RT)$$

$$\gamma_{P_2O_5} = .\ \frac{\exp\left(-\text{Ä}G°\big/RT\right) \times [\%\mathrm{P}]^2 \times f_{\mathrm{P}}^2 \times [\%\mathrm{O}]^5 \times f_{\mathrm{O}}^5}{X_{(P_2O_5)}}$$

$$2\ \mathrm{Fe}\,(l) + 1.5\ O_2\,(g) = Fe_2O_3(l) \qquad (3)$$

$$\Delta G° = -\ 815000 + 251.1\ T\ (\mathrm{J\ mol\text{-}1})$$

$$= -\ RT \ln \{a(Fe_2O_3)/h_{[\mathrm{O}]}^{1.5}\}$$

$$a(Fe_2O_3) = h_{[\mathrm{O}]}^{1.5} \times \exp(-\Delta G°/RT)$$

Estimation of activities of all the three oxides considered was carried out using the computer-based package ThermoCalc® (release *TCC-R*). The computation parameters for the slag constituents were based on the *SLAG2* database, while calculations involving the solutes in liquid steel were carried out using the *TCFE3* database.

Activity was FeO was also computed through the package FACTSage®, using appropriate database(s) for constituents in slag and steel phases. $a(P_2O_5)$ could not be computed using FACTSage® since the slag models in-built in this software did not allow considering P_2O_5 as a distinct equilibrium species. In addition, calculations for a few compositions were also carried out using the software MTDATA®. All the computations, irrespective of software used, were carried out for temperature of 1600°C (1873 K).

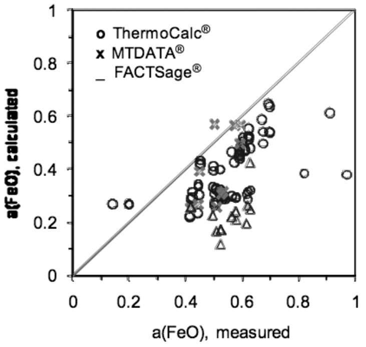
RESULTS AND DISCUSSION

Activity of FeO

The activity of FeO, obtained using the different packages, is compared with the measured values in Figure 1. All the three models under-predict a (FeO) for most of the cases. The results obtained with MTDATA® appear to be closest to the measured values, followed by those from ThermoCalc®. The computations from FACTSage® exhibit the highest deviation.

Similar comparison, but in terms of γ(FeO), have been illustrated in Figure 2. γ(FeO) computed using FACTSage® deviates the maximum from the measured values, and shows only marginal variation over the range of γ(FeO) encountered. The difference between the computed and measured values of γ(FeO), henceforth referred to *as deviation in estimation of γ(FeO)*, has been plotted in Figure 3 as a function of the activity coefficient of FeO. This figure indicates that the deviation in case of γ(FeO) estimation is non-random and increases with increasing value of γ(FeO). The trend is similar for all the thermodynamic packages considered. Hence, the computed value of activity coefficient was believed to depend on chemical parameter(s) of the system(s) investigated.

Figure 4 shows the variation of this error with FeO concentration. The extent of under-prediction appears to decrease with increasing concentration of FeO, excepting very few cases. Computations using all the three packages conform to this trend. However, the results obtained with ThermoCalc® and MTDATA® show greater scatter than FACTSage®. The effect of basicity, defined as the ratio of mass concentrations of CaO and SiO_2, on the error in γ(FeO) estimation has been illustrated in Figure 5. It can be stated that variation in basicity does not show any definite influence on the estimation of FeO activity coefficient. Similar comparisons were carried out with concentration of CaO and SiO_2 as well, but no mentionable correlation was observed.



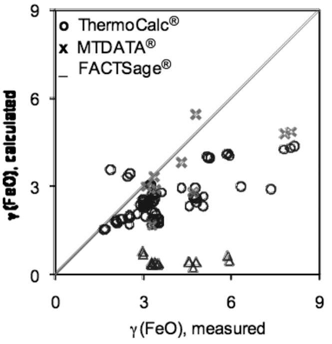
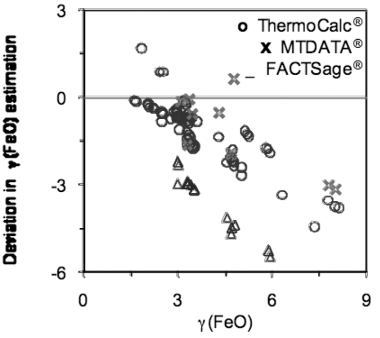


Figure 1: Activity of FeO, measured *vs*. calculated 1 using standard packages

Figure 2: Activity coefficient of FeO, measured *vs*. calculated using standard packages



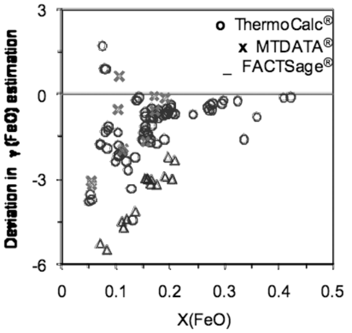
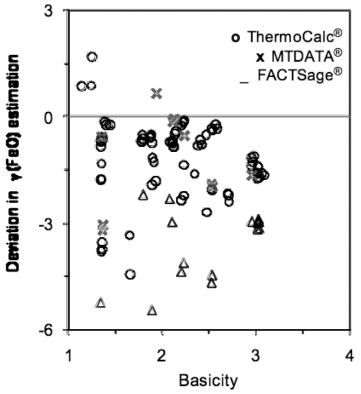


Figure 3: Variation of deviation in estimation of γ(FeO), using standard packages, with activity coefficient of FeO

Figure 4: Variation of deviation in estimation of γ(FeO), using standard packages, with its concentration

Activity of P_2O_5

The activity coefficient of P_2O_5 computed by MTDATA® agrees reasonably well with the experimental measurements, as can be seen in Figure 6. However, ThermoCalc® underpredicts $\gamma(P_2O_5)$ by as much as 5 – 7 orders of magnitude. Unlike in the case of γ(FeO), variation of $\gamma(P_2O_5)$, as well as $X(P_2O_5)$, has practically no influence on the error in its estimation, as illustrated in Figures 7 and 8.



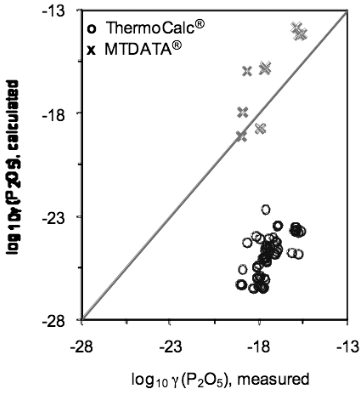


Figure 5: Variation of deviation in estimation of γ(FeO), using standard packages with basicity

Figure 6: Activity coefficient of P_2O_5, measured *vs*. calculated using standard packages

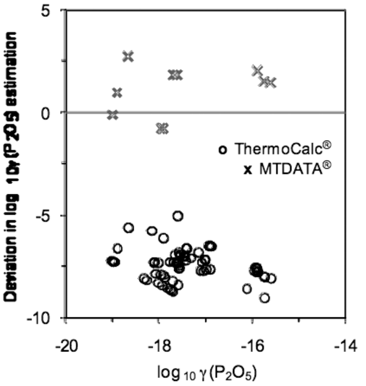


Figure 7: Variation of deviation in estimation of $\gamma(P_2O_5)$, using standard packages, with its activity coefficient

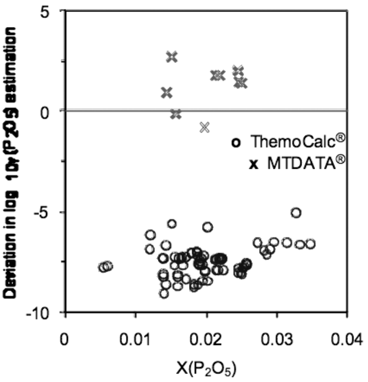


Figure 8: Variation of deviation in estimation of $\gamma(P_2O_5)$, using standard packages, with its concentration

Figure 9 shows the influence of basicity on the error in estimation of P_2O_5. The error may appear to move in the negative direction with increasing basicity, but the magnitude of scatter is also significant. The error in estimation of $\gamma(P_2O_5)$ was compared with variation in concentrations of CaO, SiO_2 and FeO as well, but no correlation could be observed. Therefore, it may be inferred that $\gamma(P_2O_5)$ computed by ThermoCalc® contains a proportionate error of 5 – 7 orders of magnitude. MTDATA®, on the other hand, tends to over-predict $\gamma(P_2O_5)$, but within 2 orders of magnitude.

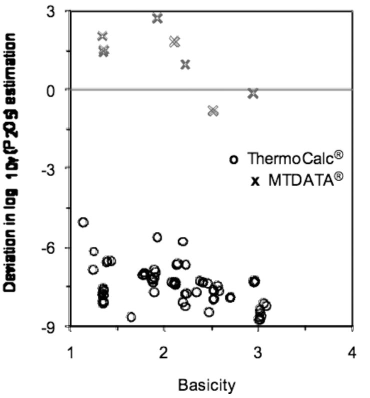


Figure 9: Variation of deviation in estimation of $\gamma(P_2O_5)$, using standard packages, with basicity

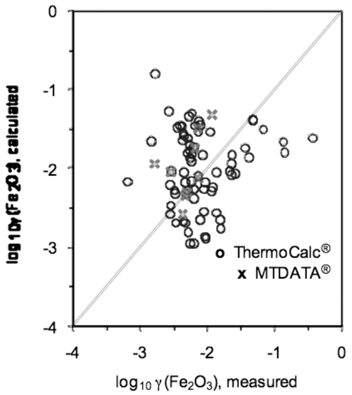


Figure 10: Activity coefficient of Fe_2O_3, measured *vs.* calculated using standard packages

Activity of Fe_2O_3

The comparison between the measured and computed values of $\gamma(Fe_2O_3)$ has been shown in Figure 10, on log-log scale. It can be seen that the computations from ThermoCalc® are almost uniformly scattered within an error band of ± 1. The results from MTDATA, though much less in number, tend to over-predict the activity coefficient of Fe_2O_3. However, the error is seen to remain within one order of magnitude.

It is further seen in Figure 11 that the error in estimation of the activity coefficient of Fe_2O_3 moves in negative direction at higher values of $\gamma(Fe_2O_3)$. An opposite trend is seen in Figure 12 where the error in $\gamma(Fe_2O_3)$ estimation, particularly the results obtained from ThermoCalc®, shows an increasing trend with concentration. This behavior may be explained by the fact that the concentration of Fe_2O_3 has a strong negative influence on its activity coefficient, as was observed by the authors earlier [3].

The variation of error in $\gamma(Fe_2O_3)$ estimation with respect to basicity has been illustrated in Figure 13. The figure tends to indicate a decreasing trend but the magnitude of scatter exceeds any systematic decrease. Hence, no definite correlation can be drawn from Figure 13. Figure 14, in contrast, clearly shows that variation in FeO concentration has no influence on the estimation of the activity coefficient of Fe_2O_3.

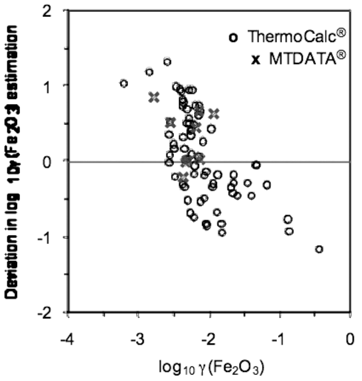


Figure 11: Variation of deviation in estimation of log10 γ (Fe_2O_3), using standard packages, with log10 $\gamma(Fe_2O_3)$

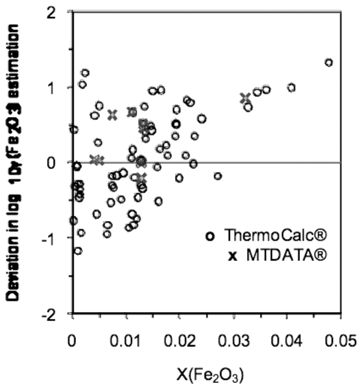


Figure 12: Variation of deviation in estimation of γ (Fe_2O_3), using standard packages, with its concentration

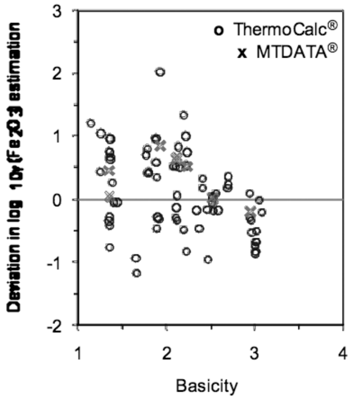


Figure 13: Variation of deviation in estimation of log10 γ (Fe_2O_3), using standard packages, with basicity

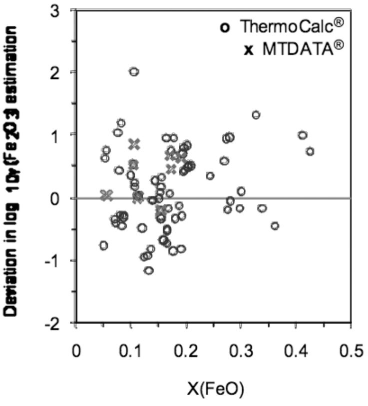


Figure 14: Variation of deviation in estimation of γ (Fe_2O_3), using standard packages, with FeO concentration

CONCLUSIONS

The estimations of the activity coefficients of FeO, P_2O_5 and Fe_2O_3, obtained from MTDATA® agree most closely with the experimental measurements. Computations using ThermoCalc® show higher extent of scatter while the results obtained from FACTSage® (for FeO) exhibit maximum deviation.

The magnitude of difference between measured and computed values of γ (FeO) decreases with increasing FeO concentration. The error for estimation of $\gamma(P_2O_5)$, however, shows no definite correlation with any compositional parameter. The amplitude of scatter in the computed values of $\gamma(Fe_2O_3)$ tends to decrease with increasing concentration, and basicity, but no definite correlation can be drawn.

ACKNOWLEDGEMENTS

The authors wish to thank Royal Institute of Technology, Stockholm, Sweden for the facilities to carry out the experiments, and Tata Steel, Jamshedpur, India for financial support towards the present work.

The authors are particularly thankful to Dr. J. Gisby at National Physical Laboratory, Teddington (UK), for his help regarding the computations using MTDATA®.

NOMENCLATURE

ThermoCalc is a trademark of ThermoCalc Software AB, Stockholm, Sweden.
MTDATA is a trademark of National Physical Laboratory, Teddington, UK.
FACTSage is a trademark of GTT Technologies, Herzogenrath, Germany.

REFERENCES

Basu, S., Lahiri, A. K. & Seetharaman, S. (2007). *Phosphorus Partition between Liquid Steel and CaO-SiO_2-P_2O_5-MgO Slag Containing Low FeO*. Metall. Mater. Trans. B, Vol. 38B (3), pp. 357–366. [1]

Basu, S., Lahiri, A. K. & Seetharaman, S. (2007). *Phosphorus Partition between Liquid Steel and CaO-SiO_2-FeO_x-P_2O_5- MgO Slag Containing 15 to 25 pct FeO*. Metall. Mater. Trans. B, Vol. 38B (4), pp. 623–630. [2]

Basu, S., Lahiri, A. K. & Seetharaman, S. (2008). *Activity of Iron 0xide in Steelmaking Slag*. Metall. Mater. Trans. B, Vol. 39B (3), pp. 447–456. [3]

Basu, S., Lahiri, A. K. & Seetharaman, S. (2007). *A Model for Activity Coefficient of P_2O_5 in BOF Slag and Phosphorus Distribution between Liquid Steel and Slag*. ISIJ Inter., Vol. 47 (8), pp. 1236–1238. [4]

Basu, S., Lahiri, A. K. & Seetharaman, S. (2008). Unpublished work. [5]